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Surface Science 357–358 (1996) 381–385

surface science

Quenching of enhanced magnetic order at Ni–Al alloy surfaces by segregated sulfur and by Ar^+ impact

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Received 15 August 1995; accepted for publication 9 February 1996

Abstract

A comprehensive study of effects of adsorbate and structural disorder on surface enhanced Curie temperature of Ni–Al solid-solutions is reported. A recently developed procedure for monitoring magnetic transitions by means of attenuations induced in the low-energy Auger electrons spectrum has been used. Sulfur segregation and argon bombardment were found to reduce the surface related Curie temperature in a similar, significant manner. Its particular dependence on coverage or ion dose is discussed in the framework of the Kirkwood correlational approximation which has been adapted for semi-infinite, spin-$\frac{1}{2}$ Ising ferromagnet with enhanced, but progressively randomized surface magnetic moments. The calculations fit the data with a single adjustable parameter reflecting the extent of S or Ar^+ induced fluctuations in the Ni surface exchange coupling.

Keywords: Auger electron spectroscopy; Ising models; Magnetic surfaces; Ni alloys

1. Introduction

The main characteristics of magnetic order at free surfaces differ remarkably from those of the underlying bulk material as studied by various surface-sensitive techniques and predicted theoretically. Recently, we reported about remarkable Curie temperature enhancements of 111 ± 4 K and 58 ± 2 K exhibited by the clean surfaces of bulk Ni–9at%Al and Ni–5at%Al alloys, respectively, as measured in a novel experiment based on the deflection of low-energy Auger electrons by fields induced by a magnetized sample [1]. Significant enhancement of exchange interactions between spins in the top layer, relative to the bulk spins which remain at a certain temperature range in the paramagnetic state, is the origin of the distinct magnetic order, observed for the first time in Gd [2]. Evidence for the surficial nature of the transitions in Ni–Al came from effects of oxygen adsorption and argon bombardment observed in preliminary experiments [1]. Thus, even very small O coverage or Ar dose led to pronounced decrease in the corresponding Curie temperature. Reductions in surface critical temperatures by surface contamination have been reported for Gd [2] and Ni–20%Fe films [3]. Spin-polarized Auger spectroscopy study of O/Fe(100) found a chemisorption-induced reduction of magnetization [4]. On the other hand, submonolayer amounts of adsorbed O_2 caused Curie

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PII S0039-6028(96)00612-7

temperature enhancement in a pseudomorphic monolayer of Fe on W(110) [5].

At least two different mechanisms have been suggested in the literature to explain observations of adsorbate-induced quenching effects on surface magnetism: (i) decrease of surface magnetic moments, or (ii) partial randomization of spin orientations due to altered exchange couplings. Reduction in Ni magnetic moment by adsorbed oxygen has been observed for the (111) surface by magnetometry [6], and predicted by electronic structure calculations for reconstructed O $p(2\times1)$/Ni(110) [7]. Minority d-band attenuation upon O adsorption on Ni(110) was detected in spin-resolved inverse photoemission (IPE) study [8], and interpreted as evidence for Ni surface magnetic moment reduction as a consequence of Ni d-hole filling. On the other hand, results obtained in IPE study of O (2×1)/Ni(110) and S (2×2)/Ni(110) show a strong ferromagnetic coupling of the adsorbates to the substrate (as in the case of Fe(001) [9]), and no reduction of magnetic moments via filling of d-holes [10]. It has been tentatively suggested that the observed IPE depolarization can be due to adsorbate-induced local changes (fluctuations) in the Ni surface exchange coupling. A similar mechanism was introduced by Kaneyoshi [11] in a statistical-mechanical theory of surface structural disorder effects on Curie temperature, which is consistent with our preliminary observations [1].

This article presents Curie temperature experimental and calculated results for Ni–Al solid-solution surfaces covered with different amounts of chemisorbed sulfur or roughened by controlled ion bombardment. Evaluation of the possible role of exchange-coupling fluctuations in the observed magnetic order quenching is a major objective of the work.

2. Experimental

Most experiments involved a large area (110) face in a polycrystalline Ni–9%Al sample described before [12]. In all experiments the sample surface was first sputter-cleaned in the UHV chamber (2×10^{-10} torr base pressure) and annealed for several minutes at ~700°C (by electron bombardment) resulting in some Al segregation at the clean surface [12]. Various sulfur segregation levels were obtained by subsequent ~900°C annealings, and estimated using Auger intensities measured for pure Ni and CdS as standards. As for the other surface modification chosen in this study, the surface was roughened gradually by applying mild 0.5 keV Ar ion bombardment for 0.5 to 2.5 min.

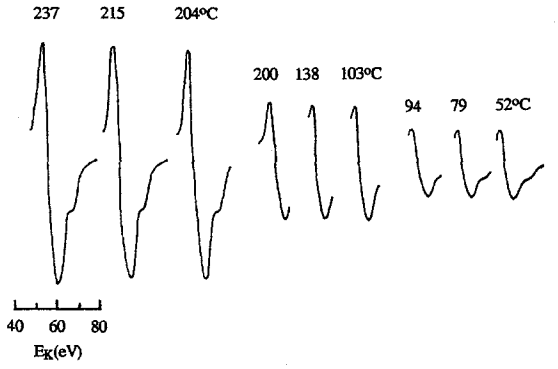

Fig. 1. The low energy portion of the Auger spectrum of Ni–9%Al (110) covered with 1.2% sulfur recorded at different temperatures (electron beam energy: 3 keV, signal modulation: 6 V). Based on hysteresis loop measured for this material, a rough estimate of stray field strength near the sample center is ~2.5 Oe, for an externally applied field of ~1.0 Oe.

Curie temperatures were measured using a new procedure based on the easy deflection of low-energy Auger electrons by Lorentz forces due to stray magnetic fields induced around the sample surface when cooled below T_C in the presence of a weak, magnetizing external field [1]. It was induced by passing electrical current through a filament adjacent to the back side of the sample, which had no direct effect on the Auger signal. This simple device was installed in a standard Auger instrument (PHI 545) with a single-pass cylindrical-mirror-electron-analyzer (CMA) used in the dN/dE mode. Deflections of Auger electrons off the CMA entrance, which are expected to start occurring just below T_C, lead to attenuated signals at the detector, as demonstrated in Fig. 1. It shows Ni MVV spectra (and Al LVV at 67 eV) of Ni–9%Al surface covered with 1.2% sulfur recorded during cooling. Two distinct magnetic transitions (discussed below) are signified by quite an abrupt attenuation of the corresponding Auger signal amplitude. Using the ratio of Ni MVV intensity to that of the higher energy Ni LMM transition is more

accurate than the use of absolute Ni MVV intensities because of cancellation of drifts in the electron beam current during the quite long experiment (deflections of the ~ 850 eV Ni LMM electrons were negligible). A plot of this ratio as a function of temperature ("attenuation plot") is a straightforward means for Curie temperature determination [1].

3. Results and discussion

Examples of attenuation plots for clean and sulfur covered Ni–9%Al surface (Fig. 2), reveal the two attenuations, which are associated with surface and bulk related magnetic transitions. The identification of the higher temperature attenuation measured for the clean surface, as due to a surface-related, enhanced magnetic transition is based mainly on the observation that chemical (or structural) modifications of the surface affected significantly the corresponding T_C^s, whereas the lower temperature transition did not change (the corresponding T_C^b agrees with the value measured for the alloy bulk using a conventional technique [13]). As can be seen, the distinct ferromagnetic order is progressively quenched until full suppression, with increasing sulfur coverage. Quenching effects of segregated S on T_C^s have

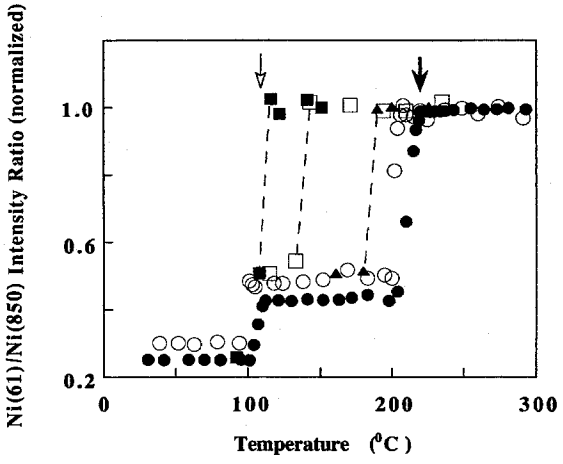

Fig. 2. Attenuation plots measured for Ni–9%Al(100): (●) clean surface, (○) covered with 1.2% S, (▲) covered with 2.0% S, (□) covered with 2.5% S, (■) covered with 3.2% S. Curie temperature for the clean surface is marked by a heavy arrow exactly above the onset of signal attenuation; the bulk Curie temperature is indicated by a light arrow.

been observed also for Ni–5%Al solid solution in the 58 degree interval between the clean surface T_C^s and T_C^b. Ar^+ bombardment of the clean surface has been also found to quench magnetic order. In particular, a gradual decrease of T_C^s towards the bulk value occurs either with increased ion beam energy [1] or with longer bombardment times. The latter results are presented below for Ni–9%Al (110) together with detailed data measured for the S covered surface, and both are compared with theoretical calculations.

Effects of structural disorder on thin film and surface magnetic properties has been studied theoretically before with probability distribution functions assumed for the exchange coupling using differential or integral operator techniques in the correlated effective-field theory [11,14]. The Kirkwood method, based on free-energy temperature expansion, is another statistical-mechanical theory that takes into account correlations and applied in various Ising-type systems. Among these, thin-film ferromagnetism has been treated by Jensen et al. [15] using the first correlational correction. A similar approach was applied to the clean surface magnetism of the Ni–Al alloys [1]. In the following it is modified to include fluctuations in the surface exchange coupling, and applied to quantitative evaluation of surface structural disorder and adsorbate effects on Curie temperature.

Starting with the spin-$\frac{1}{2}$ Ising ferromagnet model, the pth layer magnetization m_p (in the first correlational approximation) is obtained by solving self-consistently the semi-infinite system of equations [15]:

$$\begin{aligned} m_p = \tanh\Big\{ & \beta\mu_p\big(z_0 J_{p,p}\,\mu_p m_p + z_1 J_{p,p+1}\,\mu_{p+1} m_{p+1} \\ & + z_1 J_{p,p-1}\,\mu_{p-1} m_{p-1}\big) \\ & - (\beta\mu_p)^2 m_p\big[z_0 J_{p,p}^2\,\mu_p^2\big(1-m_p^2\big) \\ & + z_1 J_{p,p+1}^2\,\mu_{p+1}^2\big(1-m_{p+1}^2\big) \\ & + z_1 J_{p,p-1}^2\,\mu_{p-1}^2\big(1-m_{p-1}^2\big)\big]\Big\}. \end{aligned} \tag{1}$$

$p = 0,1,\ldots,\infty$, and μ_p denotes the magnetic moment per atom (for the surface $\mu_0 \equiv \mu_s$, for the bulk $\mu_{p\neq 0} \equiv \mu_b$). z_0, z_1 and $J_{p,p}$, $J_{p,p\pm 1}$ are coordination numbers and coupling constants in the same atomic layer and between adjacent layers, respectively, and $\beta = 1/k_B T$.

Extending this approach to the problem of local fluctuations in exchange coupling between different spin pairs at the surface (namely, a situation with a distribution of $J_s \equiv J_{0,0}$ values) requires averaging of J_s and of J_s^2 over all configurations [16]. Assuming a pure randomization effect and equality of bulk and averaged surface exchange couplings, gives $\langle J_s \rangle_r = J_s = J_b \equiv J$ and $\langle J_s^2 \rangle_r = J^2(1+\delta_s^2)$, with δ_s, the relative dispersion in J_s (or "fluctuation factor"), defined as $\sqrt{\langle J_s^2 \rangle_r - \langle J_s \rangle_r^2}\,/\langle J_s \rangle_r$. ($\delta_s$ affects only the correlation correction, proportional to β^2 in Eq. (1), and does not change T_C^s in the mean-field approximation.)

Since near the critical temperature m_p tends to zero, the system of equations (1) can be linearized,

$$m_0 = \beta\mu_s J(z_0\mu_s m_0 + z_1\mu_b m_1) - (\beta\mu_s J)^2 m_0\left[z_0(1+\delta_s^2)\mu_s^2 + z_1\mu_b^2\right],$$

$$m_1 = \beta\mu_b J(z_0\mu_b m_1 + z_1\mu_b m_2 + z_1\mu_s m_0) - (\beta\mu_b J)^2 m_1(z_0\mu_b^2 + z_1\mu_b^2 + z_1\mu_s^2), \quad (2)$$

and

$$m_p = \beta\mu_b J(z_0\mu_b m_p + z_1\mu_b m_{p+1} + z_1\mu_s m_{p-1}) - (\beta\mu_b^2 J)^2 m_p(z_0 + 2z_1) \quad \text{for } p \succ 1.$$

The dependence of T_C^s/T_C^b on the surface to bulk magnetic moment ratio μ_s/μ_b and on the fluctuation factor δ_s can be found by solving the secular equation derived from Eqs. (2) following a procedure outlined in Ref. [16]. To simplify the calculations for Ni–Al solid solutions, fluctuations due to compositional inhomogeneities, such as surface segregation gradients and possible near surface clustering are ignored, and effective coordination numbers are used for the (110) truncated structure having the bulk concentration [1]. In view of the two possible mechanisms for magnetic order quenching mentioned above, effects of variable δ_s (constant μ_s) in comparison to those of μ_s reduction (assuming $\delta_s = 0$) have been inspected. Thus, numerical calculations show that T_C^s should vary almost linearly with μ_s, whereas a Gaussian-like shape characterizes its dependence on δ_s, similar to the experimental dependence of Ni–9%Al T_C^s on sulfur concentration (Fig. 3). Indeed, for small S concentrations δ_s is expected to vary linearly ($\delta_s = k_s c_s$). As can be seen, using of

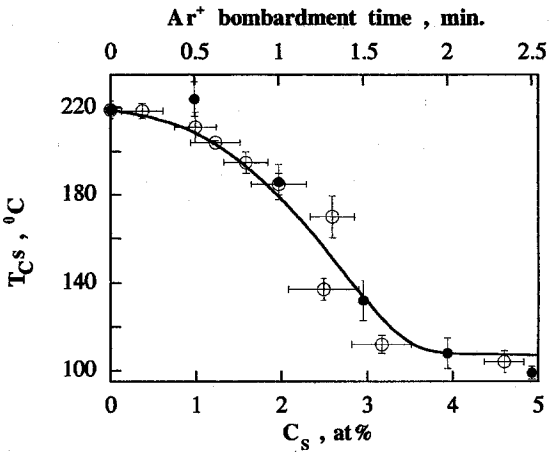

Fig. 3. Variations in the surface related experimental T_C of Ni–9%Al with sulfur concentration (○, bottom scale), and with 0.5 keV Ar ion bombardment time (●, upper scale). The solid line represents calculated T_C^s versus fluctuation factors $\delta_s = 0.33c_s$ and $\delta_s = 0.65t$, respectively, as best fits ($\mu_s/\mu_b = 1.55$ [1]).

one adjustable parameter, k_s, provides quite a good fit between calculated T_C^s values and the experimental points. This result indicates that the dominant mechanism of the T_C^s decrease by sulfur involves a gradual randomization in Ni spin orientations due to chemically induced fluctuations in J_s. A similar mechanism can be expected as result of ion bombardment which produces structural roughness at the near surface region, as discussed elsewhere [1,11]. T_C data obtained from attenuation plots measured after different Ar^+ bombardment times (but with the same ion beam parameters) are shown in Fig. 3 together with the calculated curve. The fitting procedure was similar to the previous case, namely using a linear dependence of the fluctuation factor δ_s on impingement time ($\delta_s = k_{sp}t$), since, at least initially, the abundance of structural defects is expected to increase linearly with the number of ion/surface collisions. The calculations are again consistent with the experimental results, reflecting a dominant randomization effect on Curie temperature which is similar to that of sulfur adsorption. As can be expected [16], full suppression of the distinct surface magnetic order corresponds to δ_s around unity.

To our knowledge, this is a first attempt to quantify adsorbate effects on Curie temperature in terms of fluctuations in the surface exchange coupling.

Additional investigations of the role of other adsorbates are planned. In particular, quenching of magnetic order in Ni–9%Al by oxygen, observed in our preliminary study [1], requires detailed measurements and calculations of T_C versus O coverage in order to elucidate the dominant mechanism involved.

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